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One-pot Hydrothermal Synthesis of Vanadium Dioxide Nanoparticles

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Abstract: Vanadium dioxide (VO_2) shows excellent thermochromic properties suitable for potential application in optical devices and smart windows coating. VO_2 is interesting since actual coating on glass materials is possible along with large-scale production. This paper, VO_2 nanoparticles were synthesized successfully using the sol-gel-assisted hydrothermal method. The as-prepared VO_2 nanoparticles were annealed under vacuum, and the crystal phase formation, composition, morphology, and metal-insulator phase transition properties of the nanoparticles were studied. X-ray Diffraction (XRD) spectra revealed that a purely monoclinic phase of VO_2 nanoparticles with an average crystallite size of 33.27 nm was synthesized. Scanning Electron Microscopy (SEM) micrographs also confirmed the formation of crystalline VO_2 nanoparticles. Differential Scanning Calorimetry (DSC) curve shows that the change in temperature (ΔT_c) between the exothermic and endothermic peaks is 13ºC. Moreover, Fourier Transform Infrared (FTIR) spectroscopy peaks ascertain the presence of VO_2 functional groups in the synthesized nanoparticles.

Keywords: VO_2; thermochromic; vacuum annealing; hydrothermal; smart windows.

1. Introduction

High population growth and the rapid development of the world's economy aroused greater concern for energy usage and environmental protection [1,2]. More than 40% of the world's annual energy consumption is utilized for lighting, heating, cooling, and air conditioning [3-6]. Hence, energy-saving materials for smart nano-coating in windows and solar heat control management (cooling and air conditioning) can be used as an effective technique to meet energy-saving and environmental mitigation [1,2,7,8]. Therefore, there is a growing interest in producing thermochromic materials suitable for such applications by exploiting the unique properties of nanomaterials such as vanadium dioxide and its composites [3-7,9,10].

Vanadium dioxide (VO_2) exists in different polymorphs [VO_2 (A), VO_2 (B), VO_2 (C), VO_2 (M), VO_2 (R), VO_2 (T)] and it is a well-known example of strongly correlated electronic materials [11-15]. Among these, monoclinic vanadium dioxide VO_2 (M) undergoes metal-to-insulator transition (MIT) at a temperature of (T_c) ~ 68 °C [16-18]. This thermally caused phase

transition from an insulating, low-temperature VO_2 (M) to a metallic, high-temperature VO_2 (R) is accompanied by changes in electrical, optical, and magnetic properties [16,19]. Such property endows VO_2 with solar control ability in response to environmental temperature by changing infrared transmittance, keeping visible rays, and shielding UV-ray [20-22]. Because of this anomalous behavior VO_2 is considered as a material having high potential for various applications as in optical switches [23-25], optical storage devices [26,27], thermal sensors [23,28], smart window coatings [29,30], laser protection [31,32], smart radiation devices [33,34], terahertz (THz) optical devices [35].

So far, different types of preparation methods such as spray pyrolysis [36], pyrolysis [37,38], sol-gel [29,39], hydrothermal [2,12,15,40], ball milling [41], and combustion synthesis [42] have been employed to synthesize VO_2 thin films and nanoparticles. This work employed the sol-gel-assisted hydrothermal technique to successfully synthesize monoclinic VO_2 nanoparticles due to their environmental friendliness and cost-effectiveness.

2. Materials and Methods

2.1. Materials and synthesis methods.

Analytical grade reagents such as vanadium pentoxide (V_2O_5) and hydrogen peroxide (H_2O_2, 30% wt.) were supplied by Sigma-Aldrich (South Africa) and used without further purification.

Synthesis of VO_2 nanoparticles was carried out via hydrothermal technique as described in earlier reports [12,29]. In a typical process, 2.0 g of V_2O_5 was added to 30 mL of H_2O_2 while heating at about 60 °C until the yellow color solution changed to brown-red. The resulting solution was aged for a couple of days (two days) to get the brown-red gel. It was then transferred into a 20 mL Teflon-lined autoclave, heated at 240 °C for 24 hours. The resulting blue-black precipitate was centrifuged three times after each washing with deionized water. Finally, the precipitate was collected, oven-dried at 80 °C, and annealed under a vacuum at 750 °C for 2 hours to get the black VO_2 nanoparticles.

2.2. Characterization methods.

To record the powder an X-ray diffraction (XRD) pattern of the synthesized VO_2 nanoparticles, Brucker D8 advance GER, X-ray diffractometer was employed. The spectrum was collected using CuKα1 radiation (wavelength = 1.5406 Å) at the operating voltage of 40 kV and current of 300 mA in the 2-theta range from 15°-90°. Scanning electron microscopy (SEM) images of theVO_2 nanoparticles were obtained using ZEISS, Auriga-Oxford instruments, and field emission scanning electron microscopy. The elemental analysis of the synthesized nanoparticles was carried out from the same scanning electron microscopy unit's energy dispersive X-ray spectroscopy (EDS). FTIR characterization of VO_2 nanoparticles was recorded on a Perkin Elmer Spectrum 100 spectrometer in the 4000-500 cm^{-1} range. Samples were heated from 20 ˚C-90 ˚C and cooled back from 90 ˚C-20 ˚C at a rate of 5 ˚C/min using a STA6000 temperatures scan. DSC curves were also obtained from the same instrument used to get FTIR results.

The lattice parameters for the monoclinic structure were calculated from the powder XRD pattern using the following equation [43,44]:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2\,hl\cos\beta}{ac}\right) + \frac{k^2}{b^2}, \quad (1)$$

where *a*, *b* and *c* are lattice parameters, *d* is the inter-planar spacing, and *h*, *k*, *l* are miller's indices. Crystallite size *D* was determined using Scherrer's equation:

$$D = \frac{k\,\lambda}{\beta\,\cos\theta}, \quad (2)$$

where *k* is the Scherrer's shape factor with a value of 0.9, λ is the radiation wavelength, β is the full width at half maximum (FWHM), and θ is the diffraction angle.

3. Results and Discussion

3.1. X-ray diffraction (XRD).

XRD patterns of hydrothermally synthesized VO_2 nanoparticles after annealing at 750ºC for 2 hours are shown in Figure1. Peaks of the corresponding XRD patterns are indexed to the monoclinic VO_2 (M) phase (space group: P21/c) with lattice parameters of a = 5.7517 Å, b = 4.5378 Å, c = 5.3825 Å, and β= 122.64º (JCPDS no. 00-043-1051). The XRD patterns of VO_2 (M), Figure1, shows diffraction peaks at 26.86º, 27.79º, 33.40º, 37.08º, 39.71º, 42.24º, 44.64, 53.00º, 55.55º, 57.01º, 60.52º, 64.46º, 70.52º, 72.03º, 84.09, 85.53, and 88.40 corresponding to (110), (011), (10-2), (200), (020), (210), (012), (102), (211), (112), (-311), (-131), (202), (-411), (222), (040), and (-141) patterns, respectively, with prominent peak at (011). Other phases of vanadium oxide or impurities are not detected in the spectra, and this reveals the pure phase of the VO2 (M) nanoparticle's structure.

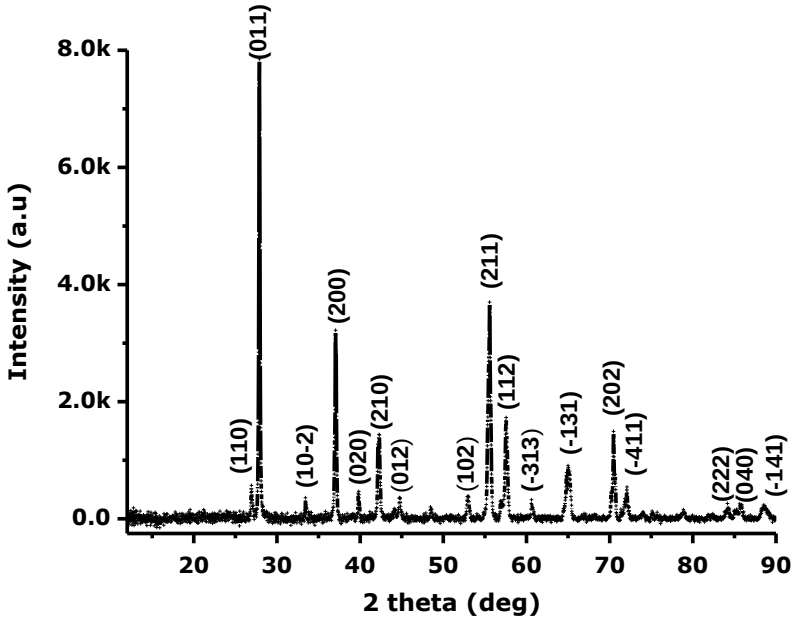

Figure 1. XRD patterns of VO_2 nanoparticles.

Table 1. Characteristics of major XRD peaks.

Miller indices	2θ (deg.)	θ (deg.)	*cos* θ	FWHM, β(deg.)	FWHM, β (10^{-2} rad.)	Crystallite size (nm)
(011)	27.79	13.895	0.9707	0.2058	0.3591	39.77
(200)	37.08	18.54	0.9481	0.2058	0.3591	40.10
(210)	42.24	21.12	0.9328	0.2744	0.4788	31.05
(211)	55.55	27.775	0.8848	0.3430	0.5988	26.17
(112)	57.01	28.505	0.8788	0.4116	0.7185	21.96
(-131)	64.46	32.23	0.8459	0.3430	0.5988	27.27

The average crystallite size was estimated using Scherrer's equation (2) to be 33.27 nm. Furthermore, from the prominent monoclinic (011) peak, the inter-planar spacing *d* is calculated using equation (1) to be 3.19 Å.

3.2. Scanning Electron Microscope (SEM).

SEM was used to study the size and morphology of the synthesized VO_2 nanoparticles. Figure 2 (a, b) shows an SEM image of the synthesized nanoparticles for 24 hours of reaction time. The magnified SEM image is shown in Figure 2 (b), revealing nanoparticles with an average crystallite size of less than100 nm, as confirmed by ImageJ analysis.

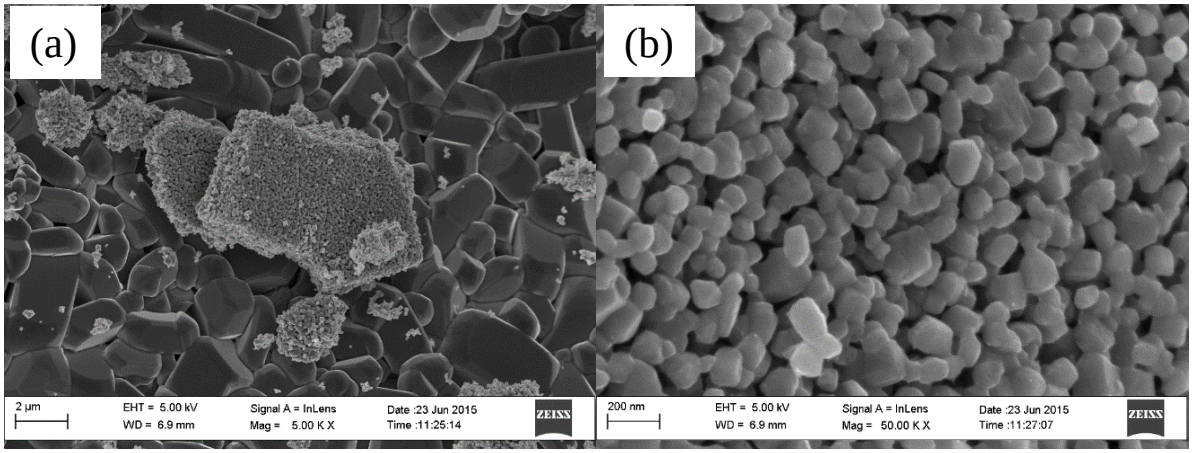

Figure 2. SEM images of VO_2 nanoparticles.

3.3. Energy-Dispersive X-ray Spectroscopy (EDS).

Figure 3 shows the EDS spectrum of VO_2 nanoparticles taken on a randomly selected specimen of the nanoparticles assumed to be representative. The EDS result indicates that VO_2 (M) nanoparticles have been successfully synthesized by the hydrothermal process. The Cu peak observed in the spectrum may be from the instrument.

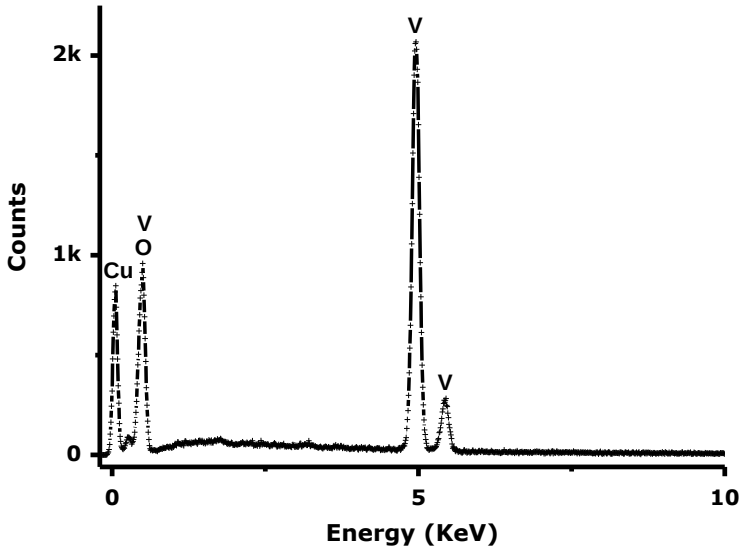

Figure 3. EDS spectrum of VO_2 nanoparticles.

3.4. Differential Scanning Calorimetry (DSC).

DSC was used to characterize the phase change temperature (T_c) properties of VO_2 nanoparticles. VO_2 sample was heated from 20˚C to 90˚C and cooled back to 20˚C at a rate of

5˚C/min. As shown in Figure 4, an endothermic peak was seen at 65˚C and an exothermic peak at 52 ˚C and the ΔT_c value is 13 ºC. This shows that the metal-insulator phase transition, which occurs at 65˚C, is slightly lower than the reported one (68.6 ˚C) [45]. Furthermore, the presence of endothermic and exothermic peaks in DSC curves for the return process also confirms the first-order phase change of monoclinic VO_2 (M) [45].

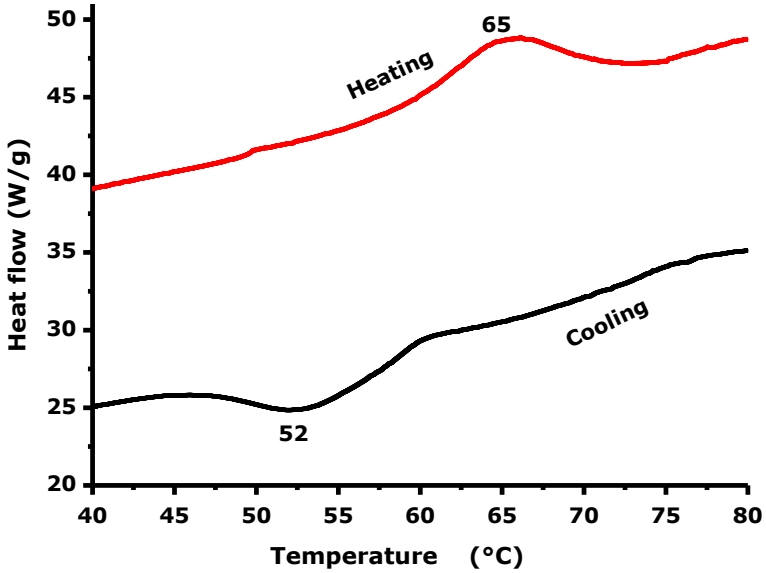

Figure 4. DSC curves of VO_2 nanoparticles.

3.5. Fourier transformed infrared spectroscopy (FTIR).

To investigate the thermochromic characteristics of hydrothermally synthesized VO_2 nanoparticles, temperature-dependent FTIR measurements of infrared transmittance between 500 and 4000 cm^{-1} were made. As observed in Figure 5, the small absorption peak at 1613.2 cm^{-1} is due to the stretching and bending vibration of H_2O. The sharp peaks of absorption at 998.2 cm^{-1}, 591 cm^{-1}, 496 cm^{-1}, and 421 cm^{-1} correspond to stretching of V=O and V–O–V coupled vibration [46].

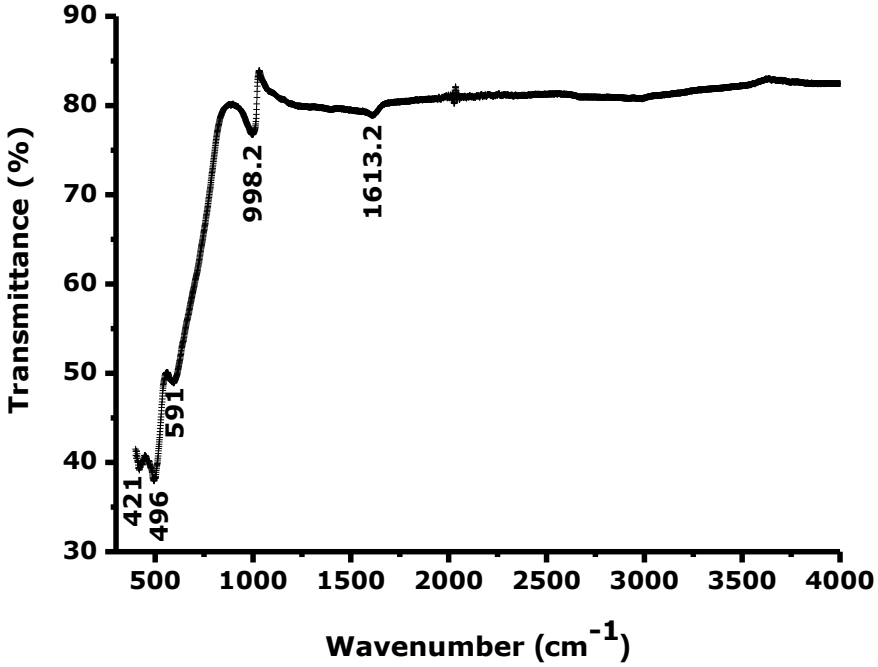

Figure 5. FTIR spectrum of VO_2 nanoparticles.

4. Conclusions

In conclusion, VO_2 nanoparticles of the monoclinic phase were successfully synthesized through sol-gel-assisted hydrothermal technique under vacuum annealing. The synthesized nanoparticles' crystallinity was confirmed from XRD spectral analysis and SEM micrographs. Moreover, the thermochromism characteristic of the as-synthesized nanoparticles was confirmed from the DSC curve, which revealed that the ΔT_c value of 13 ºC was achieved. The thermochromic property observed in the synthesized VO_2 nanoparticles, thus, is a clear indication that it suits the proposed optical and coating applications. Further optimization is required to lower the ΔT_c value by adjusting different parameters such as the pH of the solution, precursor concentration, hydrothermal reaction time, temperature, and an aging condition.

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Conflicts of Interest

The authors declare no conflict of interest.

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